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DETERMINATION OF CALCIUM-41 AND NICKEL-63 IN NPD GS CONCRETE CORE SAMPLES

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A procedure for the determination of Calcium-41 and Nickel-63 in NPD GS concrete core samples containing natural and artificially produced long lived radionuclides has been standardized. The analytes of interest were purified from other radioisotopes using a combination of procedures of solvent extraction, ion exchange and fractional precipitation. Both the Calcium-41 and the Nickel-63 in their respective purified fractions were measured by liquid scintillation counting.

1.0 INTRODUCTION

Decommissioned Nuclear Power Demonstration Generating Station (NPD GS) has become an important source of naturally aged components after 25 years of operation. As part of a program of nuclear plant aging studies/1/, concrete cores were removed from many locations at NPD GS. One of the investigations consisted of the characterization of the long lived radionuclides present in some of these core samples. Gamma spectroscopy was used to determine many of the artificially produced radionuclides/2/. However, the long lived pure beta emitters or radionuclides decaying with only electron capture process cannot easily be determined without prior separation from all other activities (natural and artificially produced). At the request of Materials Chemistry Section, method development for the isolation of calcium and nickel from the matrix and the determination of calcium-41 and nickel-63 was undertaken. This report summarizes the results of these analyses of four core samples along with the method used.

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EXECUTIVE SUMMARY

DETERMINATION OF CALCIUM-41 AND NICKEL-63 IN NPD GS CONCRETE CORE SAMPLES

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As part of a program of nuclear plant aging studies, concrete cores were removed from the decommissioned Nuclear Power Demonstration Generating Station (NPD GS) after 25 years of operation. One of the investigations consisted of the characterization of the long lived radionuclides present in some of these core samples. Gamma spectroscopy was used to determine many of the artificially produced radionuclides. However, the long lived pure beta emitters or radionuclides decaying with only electron capture process cannot easily be determined without prior separation from all other activities (artificially produced and naturally occurring). Nickel-63 ($t_{1/2}$ 100 years) and calcium-41 ($t_{1/2}$ 100,000 years) are two such radionuclide likely to be present in these cores. A procedure for the determination of these two in NPD GS concrete core samples has been standardized. The analytes, present in different core samples, were purified from other radioisotopes using a combination of procedures of solvent extraction, ion exchange and fractional precipitation. Both the calcium-41 and the nickel-63 in their respective purified fractions were measured by liquid scintillation counting.

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1.1 ACTIVATION BY ABSORPTION OF NEUTRONS

Nuclear reaction (n, τ) of an element may lead to the production of one or more excited product nuclides. These may decay by one of the many nuclear processes.

The amount of activity (A_1^*) of a product nuclide from an element is given by:

$$A_1^* = \frac{aN\delta_1\Phi\sigma(1-e^{-\cap t}i)}{At.Wt.}$$

Where

- a is the amount of element present
- N is Avogadro's number
- δ_1 is isotopic fraction of the parent nuclide
- Φ is the neutron flux
- σ is the activation cross section
- $\cap$ is the decay constant of the product nuclide
- t_1 is the irradiation time

1.1.1 Activation of Nickel

Activation of nickel will produce nickel-59 ($t_{1/2}$ 75,000 years) and nickel-63 ($t_{1/2}$ 100 years). Nickel-59 decays by electron capture process (EC) and emits low energy X-rays and Auger electrons (6-8 keV). Nickel-63 is a pure beta emitter with beta E_{max} of 65.9 kev. The time of irradiation and decay is small in comparison to the half-lives of the two nickel isotopes, therefore, their activity ratio can be estimated, as follows:

$$\frac{\text{Activity (nickel-59)}}{\text{Activity (nickel-63)}} = \frac{\delta(\text{Ni-58}) \times \sigma(\text{Ni-58}) \times \cap(\text{Ni-59})}{\delta(\text{Ni-62}) \times \sigma(\text{Ni-62}) \times \cap(\text{Ni-63})}$$

Substituting the known values for δ, σ (for thermal neutrons) and $\cap$, a ratio of 0.008 is obtained. Nickel-59 contributes very little to the activity of the nickel fraction and nickel-63 activity can be measured by liquid scintillation counting (LSC).

1.1.2 Activation of Calcium

Activation of calcium will produce calcium-41 ($t_{1/2}$ 100,000 years) and calcium-45 ($t_{1/2}$ 164 days). Calcium-41 decays by the EC process and emits low energy X-rays and Auger electrons (3-4 kev). Calcium-45 is a pure beta emitter with beta E_{max} of 257 kev. The activity ratio of the calcium isotopes can not be estimated unless irradiation history is well known due to relatively short half-life of the calcium-45. However, assuming irradiation over a period of 25 years and a 3 year cooling time before analysis, an upper limit of the activity ratio (calcium-45/calcium-41) can be estimated to be 1.5. Since the objective of this study is to characterize long-lived radionuclides, measurement of calcium-41 is of interest. Due the wide separation of the energies of the two isotopes it is possible to measure calcium-41 in the presence of other using LSC.

2.0 EXPERIMENTAL PROCEDURE

2.1 Sample Nature and Matrix

Sub-samples from concrete (cement/aggregate ratio of 0.1 and water /cement ratio of 0.52) cores from location 2, vault side, were provided for the analysis as they have been exposed to the neutrons and have been subject to possible contamination absorption/3/. The sample matrix information (chemical composition of the cement and the aggregate) supplied is listed in Table 1.

2.2 Sample Description and Initial Processing

The samples, as received, were weighed and counted for gamma emitting radioisotopes on low background hyper-pure germanium detectors coupled to an APTEC multichannel analyzer and data reduction system. The sample identification, weight and radionuclide content, as determined by the gamma spectroscopy, are listed in Table 2.

TABLE 1

ANALYTE Concentration	IN CEMENT (%)	IN AGGREGATE (%)
SiO_2	21.1	3.7
Al_2O_3	5.0	3.1
Fe_2O_3	2.5	26.2
CaO	62.2	0.8
MgO	2.6	3.2
K_2O	0.96	-
Na_2O	0.21	0.3
SO_3	2.7	-
TiO_2	-	35.0
FeO	-	28.3
MnO	-	0.17
V_2O_5	-	0.3
Cr_2O_3	-	0.1
S	-	0.28
P_2O_5	-	0.015
Cu	-	0.02
Ni	-	0.03
Loss on Ignition	1.8	-

TABLE 2

SAMPLE	SAMPLE Wt.(g)	SAMPLE ACTIVITY (nCi) (DECAY CORRECTED TO SEPT. 88) Co-60		Eu-152		Eu-154		Mn-54	
2-B6-1	1.08	70	2	6.8	0.5	0.9	0.3	1.0	0.2
2-C5-1	1.52	100	3	2.9	0.3	0.4	0.2	1.8	0.3
2-D5-1	1.79	92	3	2.6	0.2	0.3	0.1	1.1	0.2
2-C5-2	1.63	73	2	2.2	0.2	0.3	0.1	0.9	0.2

2.3 Sample Dissolution

The sample was transferred to a Teflon beaker using deionized water. Cobalt hold-back carrier was added and the mixture was treated with dilute hydrochloric acid. After the initial reaction had subsided, 10 Ml of concentrated hydrochloric acid was added to the beaker and the contents were taken to near dryness. A few milliliters of hydrofluoric acid and 10 mL of hydrochloric acid were added and the sample taken to near dryness again. The sample was then digested with repeated additions of small amount of concentrated hydrochloric acid and few drops of hydrogen peroxide till the sample dissolved. It was then taken to dryness with perchloric acid to remove fluoride ions and cooled. The calcium and nickel in the dissolved sample were measured. Nickel content of the solution was low, therefore 1 mg of nickel carrier was added to it for yield measurement.

2.4 Removal of Iron and Titanium

The dissolved sample was then taken up in 9 M hydrochloric acid and passed though a strong anion-exchange column (20 mm X 200 mm) conditioned with 9 M hydrochloric acid. The column was washed with 10 column volumes of 9 M hydrochloric acid and the effluent (containing nickel and calcium which pass through the column in hydrochloric acid medium/4/) was saved. It was taken to dryness in the presence of a 1 mL of 0.5 M oxalic acid. The residue was dissolved in 1 M hydrochloric acid + 0.5 M oxalic acid. The solution was then passed through a fresh strong anion-exchange resin column (20 mm X 200 mm) conditioned with 1 M hydrochloric acid + 0.5 M oxalic acid. Titanium is retained by the anion exchanger/5/. The column was washed with 10 column volumes of the above acid mixture and the effluent saved for Ni and Ca analysis.

2.5 Separation and Purification of the Nickel

The effluent after the removal of matrix elements, iron and titanium, was heated with enough hydrogen peroxide to destroy all of the oxalic acid. The solution was taken to near dryness to destroy any excess hydrogen peroxide present and then diluted with water. Copper carrier was added and the solution was brought to near boiling. Sufficient fresh ammonia solution was added to raise the pH of the solution to precipitate metal hydroxides (Al,Cr etc.) and then were quickly filtered off using Whatman #41 filter paper. Sodium sulfide solution was added to the filtrate to precipitate sulfides. The precipitate was filtered using Whatman #42 filter paper. The filtrate was acidified and saved for calcium analysis.

The sulfide precipitate was heated with concentrated nitric acid till it dissolved. The nickel in the solution was then extracted into chloroform as dimethylglyoxime (DMG) complex using standard procedure/6/. The nickel in the chloroform layer was back extracted with 0.1 M hydrochloric acid. The DMG purification step was repeated and the Ni-63 in the sample was determined as reported earlier/7/.

2.6 Separation and Purification of Calcium

The filtrate after the removal of nickel by sulfide precipitation was heated to dryness twice with nitric acid and taken in 0.1 M nitric acid. Barium carrier (100 mg) and 5 mL of 10 % w/v solution of potassium chromate were added. The pH of the solution was raised to 8 by adding dilute ammonia solution in order to precipitate chromates. The precipitate was filtered using Whatman #41 filter paper and discarded. The filtrate was acidified to a pH >2 and stored to allow the decay of naturally occurring activities (daughters of radium and lead). The chromate ion was reduced by the addition of sodium nitrite and the resultant tervalant chromium precipitated with the addition of fresh ammonia solution and filtered using Whatman #41 filter paper. The calcium in the filtrate was precipitated as carbonate and was filtered on Whatman #42 filter paper, washed well with water and dissolved in 0.1 M hydrochloric acid.

Barium and strontium carriers (50 mg each) were again added and a slight excess of a saturated sodium sulphate was added to precipitate barium and strontium as sulfates. The precipitate was filtered on a Whatman #42 filter paper and discarded. The calcium in the solution was precipitated again as carbonate. It was filtered, washed and dissolved in 0.1 M hydrochloric acid as before.

The purified calcium solution was taken to near dryness and residue dissolved in minimum amount (<10 mL) of deionized water and solution weighed. A known aliquot of this solution (1 g) was taken for calcium determination. Another aliquot (5 g) was used for liquid scintillation counting.

2.7 Counting of Nickel-63 and Calcium-41

The counting of nickel-63 was done using a calibrated CANBERRA PACKARD Model 2000 CA liquid scintillation counter (LSC) as described earlier/7/. Calcium-41 was counted by using a calibration curve generated using iron-55 (having similar decay process).

3.0 RESULTS AND DISCUSSION

3.1 Sample Dissolution and Matrix Element Isolation

The major elements in the concrete sample are iron (≈ 40%) and titanium (≈ 20%). Minor elements present (< 5 %) are calcium, silicon, aluminum and magnesium. The Ilmenite- Hematite aggregate is not easily dissolved and titanium tends to form insoluble hydrated oxide which only stays in solution in the presence of strong acids or complexing agents. Concentrated hydrochloric acid and/or the presence of hydrogen peroxide kept the titanium in the solution and aided the sample dissolution.

An accurate determination of nickel in the dissolved sample was difficult due to the small amount of the analyte, high salt content and the type of matrix. A large excess of nickel carrier was added to determine the final chemical yield of the purified nickel fraction. This will increase uncertainty in the nickel-63 measurements.

Initial tests, using simulated solution, showed that the removal of major matrix elements in a single step by slow hydrolysis in mildly acidic medium (pH ≈ 3) lead to erratic losses of calcium and nickel. The two stage anion exchange process, 9 M hydrochloric acid and 1 M hydrochloric acid + 0.5 M oxalic acid, was therefore chosen to remove the matrix elements.

The anion exchange resin, in 9M HCl, removes iron and cobalt along with their long lived radioisotopes iron-55 and cobalt-60 as shown by the gamma scan of the refinate. Calcium and Nickel do not form anionic complexes with chloride ions and therefore pass through the exchanger column/4/.

Titanium, forms anionic complexes with oxalate ions and can be retained on anion exchange resin in < 1.5 M HCl + 0.5 M oxalic acid/5/. Initial tests have shown that in 1 M HCl and 0.5 M oxalic acid, nickel and calcium remain soluble and pass through the anion exchange column while titanium is retained.

3.2 Purification of the Nickel Fraction

After the removal of major matrix elements and the hydroxide scavenging, nickel, zinc, manganese, copper and any traces of cobalt, which was not removed by the anion exchange resin, were isolated as sulfides. The extraction of DMG complex in chloroform from a strongly ammoniacal solution is very specific for nickel

from the above mixture. The second DMG purification cycle was used to assure a high decontamination factor from all other elements.

3.3 Purification of the Calcium Fraction

Filtrate from the removal of basic sulfides contains only alkali, alkaline earths, ammonium and magnesium ions. Radium, barium and lead are removed as chromates at ph ≈ 8. The sulfate followed by carbonate precipitation provides further decontamination from radium, barium, strontium and other ions.

3.4 Counting of Nickel-63 and Calcium-41

A standard nickel-63 solution was used to calibrate the liquid scintillation counter. A background and a standard nickel-63 solution was also counted along with the samples. The purity of the nickel fraction was ascertained by gamma counting the nickel fraction for cobalt-60 and manganese-54. The beta spectra of the sample in LSC compared well with that of the pure nickel-63 standard confirming the purity of the nickel-63 in the sample.

Calibration of liquid scintillation counter for calcium-41, decaying by EC to ground state, was done using iron-55 (decays by EC to ground state) as calcium-41 standard was not available. Both these radionuclides decay emitting low energy X-rays and Auger electrons. The window for counting calcium-41 in the liquid scintillation counter was set at 0 - 10 keV.

The results of the determination of chemical yield and activity for nickel-63 and calcium-41 are listed below in Table 3.

TABLE 3

SAMPLE	Nickel-63			Calcium-41		
	Chem. Yld. (%)	Act. (pCi)		Chem. Yld. (%)	Act. (pCi)	
2-B6-1	86	40	10	80	< 20	
2-C5-1	90	20	10	79	< 20	
2-D5-1	87	290	25	65	45	20
2-C5-2	81	120	20	73	< 20	

4.0 CONCLUSION

The two step anion exchange process adapted to remove the matrix elements iron and titanium yielded satisfactory results. These steps also provided the decontamination of analytes from other contaminants such as iron-55 and cobalt-60.

The procedure to partition and purify nickel and calcium from all other elements in the sample resulted in good chemical yield for the analytes.

The minimum detectable activity for nickel-63 of 5 pCi/sample and for calcium-41 20 pCi/sample has been established based on this procedure (chemical yield, counting aliquot and instrument performance).

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